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(54) Title: RELEASE COMPOSITIONS (57) Abstract <p>This invention relates to release compositions that comprise a radiation curable polyorganosiloxane and surface treated particulate solids. This invention also relates to a method of making a release coated substrate comprising coating a substrate with the foregoing release coating composition and curing the coating by exposing it to radiation. This invention relates to release coated articles made by the foregoing method. The invention also relates to multilayered articles comprising a first substrate, a second substrate, the foregoing release composition which has been cured by exposure to radiation, and a pressure sensitive adhesive, the release composition being adhered to the first substrate, the pressure sensitive adhesive being adhered to the second substrate, and the release composition and the pressure sensitive adhesive being adhered to each other.</p>		

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Title: **RELEASE COMPOSITIONS**

Technical Field

This invention relates to release compositions and, more particularly, to radiation curable silicone release coating compositions containing surface treated particulate solids.

Background of the Invention

5 Release coating compositions are used, for example, to coat papers or films which are used as release backing sheets (sometimes referred to as protective release sheets or release liners), overlying the pressure sensitive adhesive used in pressure-sensitive products such as labels, decals, tapes, etc. The pressure sensitive adhesive adheres to the release coated surface of the
10 release backing sheet sufficiently to enable the pressure sensitive products to be handled prior to use. When such products are used, the release backing sheet is pulled off and discarded. The exposed pressure-sensitive adhesive is pressed onto a surface where the pressure sensitive product is to be placed. Known types of release backing sheets include paper release backing sheets
15 wherein one side of the paper (the release side) is coated with a silicone polymer or copolymer.

Silicone polymers and copolymers have been used extensively as release layers on paper, film, etc., because they are inherently low in surface energy. It is desirable that silicone-coated release papers and films have a release force
20 which is low enough to enable the release backing sheet to be easily removed from a pressure sensitive adhesive coated substrate, but not so low that the release backing sheet will become separated from the pressure sensitive adhesive prior to when desired by forces normally encountered in handling and processing such as printing, die cutting and matrix stripping. "Release force" is
25 defined as the amount of force required to peel or separate the release-coated substrate from the adhesive.

The silicone polymers and copolymers (sometimes referred to as polyorganosiloxanes) used in the prior art for making release coating

compositions can be radiation cured or thermally cured. The radiation cured polymers have a number of advantages over the thermally cured polymers including better adhesion to certain substrates, higher cure processing speeds, and lower high speed release. However, the radiation cured polymers are generally significantly more costly than the thermally cured polymers. It would be advantageous to provide radiation cured polymers in a form that would permit the use of a reduced amount of polymer required for a particular use but still maintain the effectiveness of the polymer.

Polyorganosiloxanes containing functional groups which can be radiation cured in the presence or absence of a photosensitizer have been described in various patents as useful silicone release compositions. U.S. Patent 3,726,710 describes radiation-curable release compositions comprising an polyorganosiloxane having olefinically unsaturated organic groups and a photosensitizer. The composition may be applied to a paper substrate and cured by exposure to high intensity radiation to produce a release coating.

The use of polyorganosiloxanes with acrylate or methacrylate ester groups linked to SiC groups as radiation-curable coating materials for sheet-like carriers is described in, for example, U.S. Patents 3,878,263; 4,064,286; 4,963,438; 4,908,274; 4,978,726; and 5,034,491.

The use of epoxypolyorganosiloxanes in making release coating compositions is described in U.S. Patents 4,279,717; 4,313,988; 4,421,904; 4,547,431; 4,822,687; 5,217,805; 5,279,860; 5,332,797; and 5,360,833.

It is well known to use particulate solids such as fillers and pigments in polymers systems such as reinforced plastics and paints. Examples of particulate solids that have been used in making reinforced plastics include aluminum trihydrate, calcium carbonate, clays, calcium silicate, silica, talcs, mica, barytes, dolomite, and solid or hollow glass spheres. Pigments that have been used in paints include titanium dioxide, carbon black, iron oxide and phthalocyanine. These particulate solids have not been employed in the silicone release compositions of the prior art due to the fact that such particulate solids are incompatible with the silicone polymers.

U.S. Patent 3,503,782 discloses a differential release paper having a initial coating of a first release agent and a coating of a second release agent applied over a portion of the initial coat, each of the release agents having different release characteristics. The reference indicates that filler material in finely divided form can be added to the release agent coatings to control rheological properties and release characteristics. The filler materials are identified as calcium carbonate, titanium dioxide, silica, alumina, mica, calcium silicate, zinc oxide, iron oxide, polyvinylchloride, polyesters, polyamides and polycarbonates.

Summary of the Invention

This invention relates release coating compositions that comprise a radiation curable polyorganosiloxane and surface treated particulate solids. This invention also relates to a method of making a release coated substrate comprising coating a substrate with the foregoing release coating composition and curing the coating by exposing it to radiation. This invention relates to release coated articles made by the foregoing method. The invention also relates to multilayered articles comprising a first substrate, a second substrate, the foregoing release coating composition which has been cured by exposure to radiation, and a pressure sensitive adhesive, the release coating composition being adhered to the first substrate, the pressure sensitive adhesive being adhered to the second substrate, and the release coating composition and the pressure sensitive adhesive being adhered to each other.

Description of the Preferred Embodiments

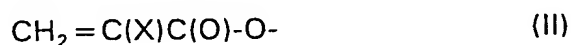
The radiation-curable polyorganosiloxanes that can be used with this invention can be any radiation-curable polyorganosiloxane known in the art. These compounds include radiation-curable epoxypolyorganosiloxanes. These compounds are sometimes referred to as radiation-curable polysiloxanes or silicones, and include, in particular, radiation-curable polydimethylsiloxanes.

The polyorganosiloxanes may contain acryloxy groups, methacryloxy groups, or combinations thereof. A variety of such acryloxy or methacryloxy containing polyorganosiloxanes can be used with the inventive release coating

compositions. In one embodiment, the polyorganosiloxane compounds containing acryloxy and/or methacryloxy groups which can be utilized in the present invention may be represented by the formula



wherein in Formula (I), each R is acryloxy, methacryloxy, a non-substituted monovalent hydrocarbon group containing from 1 to about 20 carbon atoms or a substituted monovalent hydrocarbon group wherein the substituents are selected from the group consisting of chloro-, fluoro-, cyano-, amido-, nitro-, ureido-, isocyanato-, carbalkoxy-, hydroxy-, acryloxy-, methacryloxy-, etc.; n has an average value of about 1.8 to about 2.2; and m has an average value greater than 2, and in one embodiment greater than about 25, and in one embodiment from about 100 to about 500; the polyorganosiloxane containing an average of at least one R group which contains an acryloxy or methacryloxy group, namely,

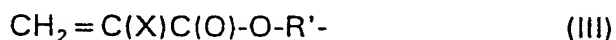


wherein in Formula (II), X is hydrogen or methyl. The substituents represented by R in Formula (I) include, for example, monovalent aliphatic groups such as methyl, ethyl, propyl, hexyl, etc.; monovalent cycloaliphatic groups such as cyclohexyl, cyclopentyl, etc.; aryl groups such as phenyl, methylphenyl, benzyl, etc.; alkenyl groups such as vinyl, allyl, 3-butenyl, etc. Examples of R groups which are substituted hydrocarbon groups include pentachlorophenyl, aminomethyl, 3-aminopropyl, etc.

Each acryloxy or methacryloxy group is attached to the siloxane backbone through a carbon-to-silicon bond or a carbon-oxygen-silicon bond. More often, there are present an average of from about 2 to about 25, and in one embodiment from about 2 to about 10 of the R groups containing an acryloxy or methacryloxy group. Alternatively, the polyorganosiloxane compounds containing acryloxy and/or methacryloxy groups useful in the present invention may be defined as containing from about 3% to about 75% by weight of acryloxy or methacryloxy groups, and in one embodiment about 3% to about 50% by weight of the acryloxy or methacryloxy groups. The polyorganosiloxanes that are useful with this invention have an average

molecular weight of from about 1000 to about 20,000, and in one embodiment about 3500 to about 8000. Polyorganosiloxanes of higher molecular weight also may be used.

Typically, the R groups in Formula (I) have the structure



wherein in Formula (III), R' is a divalent hydrocarbon group of from 1 to about 15 carbon atoms or an oxyalkylene group containing from 1 to about 4 carbon atoms in the alkylene moiety.

The polyorganosiloxanes containing the acryloxy or methacryloxy groups of Formula (III) can be prepared, for example, by reacting siloxane containing hydroxyl groups or epoxy groups with acrylic acid or methacrylic acid. The siloxanes containing hydroxyl groups may be prepared by reacting a reactive siloxane (e.g., containing halogen) with a polyhydroxy compound such as ethylene glycol, propylene glycol, glycerol or pentaerythritol.

The polyorganosiloxanes described above may be linear or branched and in one embodiment they are substantially linear. As will be recognized by those skilled in the art, the polyorganosiloxanes of Formula (III) will also have an appropriate number of end-capping units, $\text{R}_3\text{SiO}-$, at the terminals of the molecule where R is as previously defined.

The polyorganosiloxanes containing acryloxy and/or methacryloxy groups as described above are generally fluids which have viscosities in the range of from about 25 cps to 10,000 cps. Polyorganosiloxanes of the type described above are known in the art, and various methods for producing such polyorganosiloxanes are described in U.S. Patents 3,878,263; 4,064,286; 4,301,268; 4,306,050; 4,908,274; 4,963,438; 4,978,726; and 5,034,491, which are hereby incorporated by reference for their disclosure of acrylate or methacrylate containing polyorganosiloxanes and methods of preparing polyorganosiloxanes containing acryloxy and/or methacryloxy groups that are useful in the compositions of the present invention.

Polyorganosiloxanes containing acryloxy and/or methacryloxy groups are available commercially from, for example, Goldschmidt Chemical

Corp., Hopewell, Va. Goldschmidt's silicone acrylate series include dimethylpolysiloxanes available under the general trade designation Tergo® RC, and more particularly, under designations such as RC 450, RC 450N, RC 706, RC 707, RC 710, RC 720 and RC 726. Some of these polyorganosiloxanes are of the type prepared by the reaction of acrylic acid or methacrylic acid with dimethylpolysiloxane containing hydroxyl groups or epoxy groups. A useful polyorganosiloxane containing epoxy groups is available from General Electric under the designation UV 9315.

In one embodiment, the radiation-curable silicone release composition which can be used comprises an polyorganosiloxane containing acryloxy or methacryloxy groups, and further comprises an acrylated or methacrylated organic polyhydroxy compounds or polyamino compounds. The weight ratio of polyorganosiloxane to acrylated and methacrylated polyhydroxy and polyamino compounds may vary over a wide range. Thus, the mixture may comprise from about 2% to about 90% by weight of the polyorganosiloxane and from about 10% to about 98% by weight of the acrylated or methacrylated polyhydroxy and/or polyamino compounds. In one embodiment, this mixture contains about 2% to about 7% of the polyorganosiloxane and from about 93% to 98% by weight of the acrylated or methacrylated polyhydroxy and/or polyamino compounds.

The inventive release compositions may comprise a mixture of more than one acrylated or methacrylated organic polyhydroxy compound or polyamino compound. Such mixtures may comprise two or more derivatives derived from polyhydroxy compounds, two or more compounds derived from polyamino compounds, mixtures of one or more compounds derived from a polyhydroxy compound and one or more compounds derived from a polyamino compound. Thus, in one embodiment, the mixture comprises a mixture of from about 40% to about 70% by weight of at least one acrylated or methacrylated polyamine oligomer, and from about 30% to about 60% by weight of at least one acrylated or methacrylated polyhydroxy compound.

In one embodiment, a portion of the acrylated or methacrylated compound may be replaced by a liquid monoacrylate ester. For example, from about 1% to about 20% by weight of the polyacrylate in the above mixtures may be replaced by a liquid monoacrylate ester to modify the properties of the radiation-curable silicone release composition and, in some instances, the properties of the radiation-cured release composition. The liquid monoacrylate esters generally are characterized by a low viscosity such as from about 1 to about 50 cps at 25°C, and these monoacrylate compounds are useful to improve the fluidity of the curable release compositions of the invention. Examples of such liquid monoacrylate esters include ethyl acrylate, butyl acrylate, 2-ethylhexyl acrylate, allyl acrylate, n-amyl acrylate, benzyl acrylate, cyclohexyl acrylate, diethylaminoethyl acrylate, 2-ethoxyethyl acrylate, n-lauryl acrylate, n-octyl acrylate, octadecyl acrylate, etc., the corresponding methacrylates and mixtures thereof.

The monoacrylate and monomethacrylate compounds do not form a network when polymerized by radiation. However, the monoacrylates do modify the network formed by the polyfunctional acrylates. These monoacrylate compounds normally copolymerize with the polyfunctional acrylates and methacrylates.

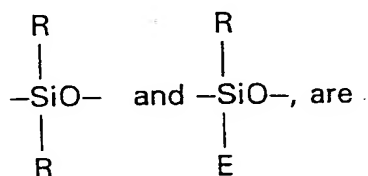
In one embodiment, the polyorganosiloxane is a curable epoxypolyorganosiloxane. These compounds can be represented by the formula:



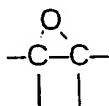
wherein in Formula IV: each R is independently a hydrocarbon group of 1 to about 18 carbon atoms, and in one embodiment 1 to about 6 carbon atoms; E is a monovalent epoxy containing hydrocarbon group; G is a silyl group represented by the formula $\text{R}_3\text{Si}-$ or $\text{R}_2\text{ESi}-$ wherein R is as defined above; a is a number in the range of about 10 to about 300, and in one embodiment about 50 to about 200; and b is a number in the range of about 2 to about 10.

Illustrative examples of the hydrocarbon group R in Formula (IV) include alkyl groups such as methyl, ethyl, propyl, isopropyl, butyl, isobutyl, tert-butyl, hexyl, octyl and octadecyl; aryl groups such as phenyl, naphthyl and

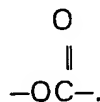
bisphenyl; alkaryl groups such as tolyl and xylyl; aralkyl groups such as phenylmethyl, phenylpropyl and phenylhexyl; and cycloaliphatic groups such as cyclopentyl, cyclohexyl and 3-cyclohexylpropyl; and ether oxygen- or ester oxygen-containing groups such as ethoxypropyl, butoxybutyl, and ethoxycarbonylpropyl and the like. The siloxane groups,



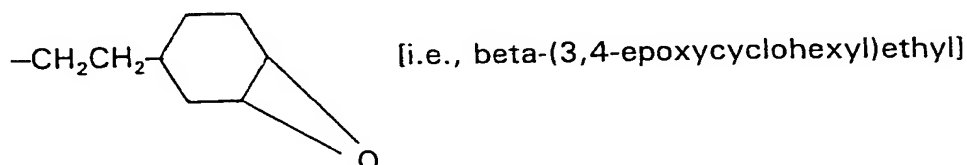
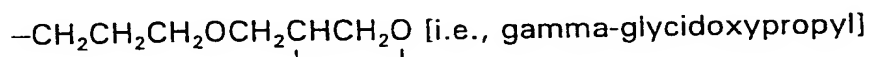
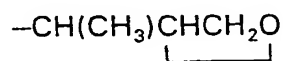
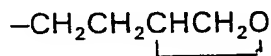
ordered or randomly arranged in the epoxypolyorganosiloxane and the epoxy-containing hydrocarbon group, E, contains at least one epoxy group,

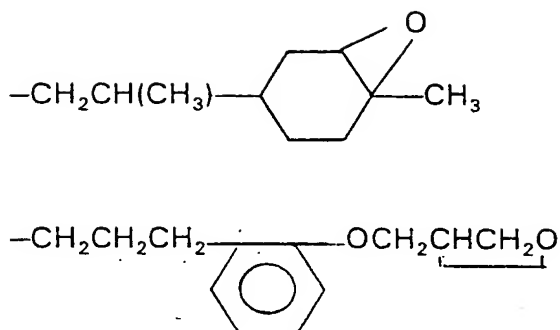


the remainder being comprised of carbon and hydrogen and, in addition to the oxirane oxygen, this group may optionally contain ether, $-\text{O}-$, or carbonyl oxygen, e.g.,



Illustrative examples of E include:





In the above epoxy-containing hydrocarbon group, the epoxy group is preferably located at the terminal position but it need not be a terminal group.

In one embodiment, the epoxypolyorganosiloxanes are those where R is methyl, and E is beta-(3,4-epoxycyclohexyl)ethyl or gamma-glycidoxypropyl.

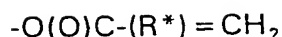
The epoxypolyorganosiloxanes can be prepared by many methods known in the art such as the chloroplatinic acid catalyzed addition reaction of hydrosiloxanes, containing the $\equiv\text{SiH}$ reactive group, with aliphatically unsaturated epoxy compounds, epoxidation of vinyl or like unsaturated siloxanes and Grignard type reactions as for example described by E.P. Plueddemann and G. Fanger, J. Am. Chem. Soc. 81, 2632-35 (1959), and U.S. Patents 4,279,717; 5,258,480; 5,360,833; 5,391,676; and 5,397,813 which are incorporated herein by reference.

An example of a useful epoxypolyorganosiloxane that is commercially available is UV 9400 which is available from GE Silicones.

In one embodiment, the inventive release coating composition further comprises an organosiloxane copolymer represented by the formula



wherein in Formula (V), each R is independently a hydrocarbon group or a group represented by the formula



wherein R^* is hydrogen or a methyl or ethyl group; x is a number from about 0.25 to about 75, and in one embodiment from about 1 to about 75, and in one embodiment about 3 to about 26; y is a number from about 1 to about 56, and in one embodiment from about 10 to about 20; and the ratio of x to y is from about 0.3:1 to about 1.5, and in one embodiment about 0.3:1 to about 1.3:1, and in one embodiment 0.7:1 to about 1.5:1, and in one embodiment about 0.8:1, and in one embodiment about 0.65:1. These compounds can have number average molecular weights of up to about 10,000. Each R in Formula (V) can be the same or different and can contain up to about 10 carbon atoms, and in one embodiment about 2 to about 6 carbon atoms. Each R can be independently an alkyl group such as methyl, ethyl, isopropyl, butyl or hexyl; an alkenyl group such as vinyl, allyl or hexenyl; an aryl group such as phenyl, tolyl or xylyl; an aralkyl group such as beta-phenylethyl or beta-phenylpropyl; a cycloaliphatic group such as cyclopentyl, cyclohexyl or cyclohexenyl; or an acrylic group such as acrylate or methacrylate. The inventive release compositions may contain a copolymer of the type represented by Formula (V) at a concentration of up to about 90% by weight based on the total weight of inventive release compositions.

Copolymers of the type represented by Formula (V) are sometimes referred to in the art as MQ resins due to the fact that the group R_3SiO is a monofunctional group and the group $SiO_{4/2}$ is a quadrafunctional group. Copolymers of this type are well known in the art and described, for example, in U.S. Patent 2,676,182, which is incorporated herein by reference for its teachings regarding the preparation of such copolymers. Briefly summarized, these copolymers can be prepared by acidifying an aqueous solution of sodium silicate using a mixture of hydrochloric acid and isopropanol. The resulting acidic silica hydrosol is then treated with a source of $R_3SiO_{1/2}$ siloxane units, such as R_3SiOCH_3 , R_3SiCl or $R_3SiOSiR_3$, dissolved in a mixture of isopropanol and xylene. The molar ratio of $R_3SiO_{1/2}$ units to the $SiO_{4/2}$ units derived from the

sodium silicate is generally from about 0.3:1 to about 1.5:1, and in one embodiment about 0.3:1 to about 1.3:1. After being heated, the reaction mixture is cooled, separated into an aqueous phase, which is discarded, and a nonaqueous phase comprising the siloxane copolymer. The siloxane copolymer is further washed with water to reduce its acid number and to remove water-soluble components, such as isopropyl alcohol. In one embodiment, siloxane copolymer has sufficient acid remaining therein to provide an acid number of from about 0.2 to about 2.

An example of a commercially available copolymer of the type represented by Formula (V) in which the R group is vinyl is available from GE Silicones under the trade designation SL 5030. Another example of a copolymer of this type that is available is UV 9430 which is available from GE Silicones. Another example is the organosiloxane copolymer present in RC-708, which is a product of Goldschmidt Chemical that is believed to be a mixture of a dimethylpolysiloxane and an organosiloxane copolymer of the type represented by Formula (V). Other commercially available copolymers that are useful include: SL4406, SL5070 and SL6030 available from GE Silicones; Syl-Off 7602, 7679, Q2-7069 and 7810 available from Dow Corning; PC-290 available from Rhone-Poulenc; and VP1517, CRA-17 and CRA-64 available from Wacker. Solvent-borne versions of these copolymers are available from PCR Inc. under the designations MQV-4, MQOH-4, MQOH-6 and MQDH-1.

The inventive release compositions may contain at least one photoinitiator. The amount of photoinitiator included in the release compositions may range from about 0% to about 10% by weight, and in one embodiment from about 0.5% to about 5% by weight, based on the total weight of the release composition (excluding the weight of the surface treated particulate solids). A photoinitiator is incorporated into the curable release compositions when compositions are to be cured by exposure to non-ionizing radiation such as ultraviolet light. Photoinitiators are not required when the curable silicone is cured by electron beam radiation. Examples of photoinitiators which may be used in combination with ultraviolet light includes, for example, benzyl ketals,

benzoin ethers, acetophenone derivatives, ketoxime ethers, benzophenone, benzo or thioxanthenes, etc. Specific examples of photoinitiators include: 2,2-diethoxyacetophenone; 2- or 3- or 4-bromoacetophenone; benzoin; benzophenone; benzoquinone; 1-chloroanthroquinone; p-diacetyl-benzene; 9,10-dibromoanthracene; 1,3-diphenyl-2-propanone; 1,4-naphthyl-phenyl ketone; 2,3-pentenedione; propiophenone; chlorothioxanthone; xanthone; and mixtures thereof. Examples of commercially available photoinitiators that can be used are available from the Ciba Geigy Corporation of Hawthorne, N.Y. under the tradename of Durocure 1173, and General Electric Company under the name UV9380C.

The particulate solids that are useful are surface treated particulate solids. These include surface treated particulate fillers and pigments. Examples include surface treated aluminum trihydrate, calcined clay, talc, calcium carbonate, ceramic spheres, glass spheres, silica, and the like. The surface treatment can be with vinyl or epoxy silane, as well as other functional silanes that are effective in rendering the surface of the particulate solids hydrophobic and compatible with the polyorganosiloxane. Examples of commercially available surface treated particulate solids that can be used include Translink 77 (a product of Engelhard identified as a vinyl treated calcined clay) and Martinal 104LE (a product of United Minerals identified as an epoxy silane treated aluminum trihydrate).

The surface treated particulate solids can be prepared by contacting such solids with a coupling agent, reactive diluent, or mixture thereof. Examples of useful coupling agents include the glycol ethers known in the art such as dipropylene glycol n-butylether. Examples of reactive diluents include n-butylacetate and diacetone alcohol. The contacting of the particulate solids and the coupling agent or reactive diluent may be effected using standard mixing techniques at a temperature in the range of about 15°C to about 40°C, and in one embodiment about 20°C to about 30°C. The weight ratio of solids to coupling agent or reactive diluent can be in the range of 5 to about 30, and in one embodiment about 15 to about 25.

The mean diameter of the surface treated particulate solids is generally in the range of about 0.1 to about 30 microns, and in one embodiment about 1 to about 20 microns, and in one embodiment the mean diameter about 2.3 microns, as measured using laser light scattering. In one embodiment, the mean diameter of about 90% of the particulate solids is less than about 8 microns, and about 100% of the solids has a mean diameter less than about 30 microns.

The surface treated particulate solids can be combined with the polyorganosiloxanes of the inventive compositions using standard mixing techniques. These materials can be mixed at a temperature in the range of about 15°C to about 40°C, and in embodiment about 20°C to about 30°C. The surface treated particulate solids are used in the inventive release coating compositions at an effective concentration to enhance rheological properties of such release coating compositions and generally at a concentration in the range of about 5 to about 40 percent by weight, and in one embodiment about 10 to about 20 percent by weight, based on the total weight of the release composition.

The surface treated solids containing radiation-curable release compositions of the present invention are applied to the desired substrate as a coating by any conventional means known in the coating art such as roller coating, curtain coating, brushing, spraying, reverse roll coating, doctor knife, dipping, die coating, offset gravure techniques, etc. The liquid being applied to the substrate may be heated or cooled to facilitate the coating process and to alter the depth of the penetration of the liquid coated into the substrate prior to curing.

A variety of substrates can be coated with the treated solids containing radiation-curable release compositions of the present invention, and these compositions can be applied to any substrate when it is desirable to modify the release properties of a surface of the substrate. For example, the compositions of the present invention can be employed to form release coatings on substrates such as paper, vinyl, polyvinyl chloride films, polyester films,

polyolefin films, non-woven fabrics, glass, steel, aluminum, etc. Included among the types of paper which can be used is paper, clay coated paper, glassine, polymer coated paper, paperboard from straw, bark, wood, cotton, flax, cornstalks, sugarcane, bagasse, bamboo, hemp, and similar cellulose materials prepared by such processes as the soda, sulfite or sulfate (Kraft) processes, the neutral sulfide cooking process, alkali-chlorine processes, nitric acid processes, semi-chemical processes, etc. Although paper of any weight can be employed as a substrate material, paper having weights in the range of from about 20 to about 150 pounds per ream are useful, and papers having weights in the range of from about 30 to about 60 pounds per ream are presently preferred. The term "ream" as used herein equals 3000 square feet. Examples of specific papers which can be utilized as substrates in preparing the composite laminates of the present invention include Kraft papers such as 40-pound and 50-pound bleached Kraft papers; 41-pound offset grade bleached Kraft paper; etc. The present invention is particularly useful in providing release characteristics to paper and polymeric films.

The amount of solids-containing radiation-curable release composition of the invention applied to the various substrates varies depending upon the characteristics of the substrate, the properties desired in the release coating, the radiation source utilized, and the particular formulation of the release composition. If an excess of the coating composition is applied to the substrate, the physical characteristics of the substrate may be affected in an undesirable manner. Also, for economic reasons, it is normally desired to apply the lowest amount of coating to obtain the desired result. Thus, applied coating weights may, depending on the substrate and intended use, range from about 0.1 to about 10 or more grams per square meter (gsm). In general, when it is desired to produce a release-coated paper useful as a protective cover for a pressure-sensitive adhesive tape, the applied coating weights are from about 1 to about 3 gsm. At these levels, desirable high release characteristics are obtained without distorting the essential components of the substrate so that a flat construction which has good performance in the end use can be produced.

5 The solids containing release compositions of the present invention can be cured by exposure to known forms of ionizing or actinic non-ionizing radiation. Useful types of radiation include ultraviolet light, electron beam, x-ray, gamma-ray, beta-ray, etc. If ultraviolet light is to be used as the form of radiation, a photoinitiator such as described above is included in the curable release composition. One of the advantages of using radiation to effect cure of the composition is that polymerization takes place rapidly at ambient temperature, and heating is not necessary. The equipment for generating these forms of radiation are well known to those skilled in the art.

10 Curing of the solids containing release compositions of the present invention can be effected in a continuous manner by passing the release-coated substrate through radiation equipment which is designed to provide the coated substrate with sufficient residence time to complete the cure of the coating. Curing may be effected in an air atmosphere or in an inert atmosphere such as
15 nitrogen or argon. An inert atmosphere is preferred. The length of exposure necessary to cure the release compositions of the present invention varies with such factors as the particular formulation used, type and wavelength of radiation, dose rate, energy flux, concentration of photoinitiator (when required), the atmosphere and thickness of the coating. A total dosage of from about 0.2
20 to about 10 megarads, and in one embodiment about 1 to about 2 megarads, is typically sufficient to cure the inventive silicone release compositions. Generally, the time of exposure that is required is about 0.1 to about 3 seconds, and in one embodiment about 0.5 to about 1 second. The actual exposure time required to give proper curing for various release compositions can be readily
25 determined by one skilled in the art with a minimum of experimentation. In one embodiment, the dosage is about 50 to about 400 mj/cm², and in one embodiment about 80 to about 400 mj/cm².

30 Substrates which have been coated with the solids containing release compositions of the present invention and cured exhibit desirable high and controlled release properties, the release coating is resistant to moisture and solvents, and the coating is thermally stable. As indicated previously, a

substrate which is coated with the cured release composition of the present invention can be used as a protective covering for a second substrate having pressure-sensitive adhesive coating on its surface. The protective covering is normally applied to the adhesive-coated substrate by bringing the two coated
5 substrates into surface-to-surface contact with the release coating on the first substrate in contact with the pressure-sensitive adhesive on the second substrate. Application of a slight pressure is usually effective to cause the coated substrates to adhere together forming a four-layered laminate. When a coated release paper prepared in accordance with the present invention is used
10 as a protective covering on a pressure-sensitive adhesive tape, a desirable high-release force is required before the release-coated paper will separate from the adhesive tape, and there is little transfer of the silicone release coating from the paper onto the adhesive. The composition of the present invention is useful particularly to prepare coated papers which are useful in high-speed equipment
15 such as labeling equipment where a high release force is desired at the high peel rates utilized.

Accordingly, the present invention contemplates the use of the compositions described above in the preparation of multi-layer articles or constructions comprising (a) a first substrate; (b) a second substrate; (c) a
20 release layer comprising the solids-containing release coating composition of this invention which has been cured by exposure to radiation; and (d) a layer comprising a pressure-sensitive adhesive composition, wherein the release layer (c) is interposed between the first substrate and the layer of pressure-sensitive
25 adhesive and is preferentially adherent to the first substrate, and the pressure-sensitive adhesive layer (d) is interposed between the release layer and the second substrate and is preferentially adherent to the second substrate. Additional layers can be interdispersed between the first substrate and the layer of pressure-sensitive adhesive and between the second substrate and the release
30 layer to provide additional desirable properties such as increased strength, increased dimensional stability, etc. As in other applications described above, the first and second substrates may comprise a variety of materials including

paper, polyolefins, vinyl, polyester, aluminum, etc., although substrates such as vinyl, polyolefins and paper are preferred.

With reference to the multi-layered articles or constructions utilizing at least one layer of a pressure-sensitive adhesive composition, any pressure-sensitive adhesive composition known in the art can be utilized. Such adhesive compositions are described in, for example, "Adhesion and Bonding", Encyclopedia of Polymer Science and Engineering, Vol. 1, pages 476-546, Interscience Publishers, 2nd Ed. 1985. Such compositions generally contain an adhesive polymer such as natural, reclaimed or styrene-butadiene rubber, styrene butadiene or styrene isoprene block copolymers, polyisobutylene, poly(vinyl ether) or poly(acrylic) ester as a major constituent. Other materials may be included in the pressure-sensitive adhesive compositions such as resin tackifiers including, for example: rosin esters, oil-soluble phenolics, or polyterpenes; antioxidants; plasticizers such as mineral oil or liquid polyisobutylenes; and fillers such as zinc oxide or hydrated alumina. The selection of the pressure-sensitive adhesive to be used in any particular multi-layer article or construction is not critical to this invention, and those skilled in the art are familiar with many suitable pressure-sensitive adhesives. However, as known to those skilled in the art, the pressure-sensitive adhesive and the release layer should not chemically react.

The solids containing radiation-curable release compositions of this invention provide cured coatings and films which have excellent release characteristics, and when applied to a substrate such as paper, the coated paper exhibits improved dimensional stability under varying conditions such as temperature, humidity, aging, etc. A particularly desirable property of substrates such as paper which have been coated with the release compositions of this invention and constructions such as labels prepared therefrom is that they lay flat and remain flat over time, even when exposed to moisture and low or high temperatures.

The surface treated particulate solids used with the inventive release compositions provide such compositions with flexibility in the control of

5 rheological properties. These compositions are characterized by enhanced misting control, better fiber coverage so that less costly substrate materials can be used, enhanced adhesion and release properties, and die cutting fracture resistance. The use of treated particulate solids in the inventive compositions provides for significant cost reductions due to the ability to use reduced levels of costly polyorganosiloxane polymers in such compositions, and the enhanced fiber coverage provided by the inventive release compositions further reduces the amount of release coating composition required for many applications.

10 The inventive release compositions are particularly advantageous when the polyorganosiloxane is a radiation-curable epoxy polyorganosiloxane due to the fact that such compositions can be used with conventional substrates such as conventional release liner paper. When the surface treated particulate solids are not used, specially designed substrates are required for use with such epoxy polyorganosiloxanes.

15 In one embodiment, use of the surface treated particulate solids with epoxy polyorganosiloxanes or acrylic polyorganosiloxanes provides the resulting inventive release compositions with reduced adhesive detackification characteristics.

Example 1

20 Release coating compositions having the formulations indicated below are prepared (all numerical values in the table below being in parts by weight):

Ingredients

Sample

AB

25 UV 9500 (product of GE identified as a UV curable polyorganosiloxane)

50

65

UV 9430	35	35
Translink 77	15	0

Sample A is representative of the invention and Sample B is a control provided for purposes of comparison. Sample A is made by mixing UV 9500 and UV 9430 at room temperature until a uniform mixture is formed and then adding the Translink 77 and mixing for 5-10 minutes until a uniform mixture is obtained. Sample B is made by mixing the UV 9500 and UV 9430 at room temperature until a uniform mixture is obtained.

Release coated liners are made using Samples A and B. Samples A and B are coated on the felt side of 55 inch wide samples of JR Camus MG Sheet (a product of James River identified as a 33# machine glazed red liner paper) under the conditions indicated below. The JR Camus MG sheet is a conventional release liner paper. Sample A is also coated on a 55 inch wide sample of 42# Otis UV 350 paper which is a product of Otis Specialty Papers identified as 42# premium paper specially designed for use with epoxy-based UV silicones. The coating conditions are as follows:

Line speed:	800 fpm
Coat weight:	1.3 gsm
Coating temperature:	70°F
Coating roll temperature:	70°F
Radiation type:	600 watt fusion "H" bulb
Dose:	150 mj/cm ²

Laminate samples are made by adhering the release coated liner samples to the adhesive surface of adhesive coated paper facestocks. The adhesive is a solvent acrylic adhesive. The adhesive coated facestocks are prepared by casting the adhesive on the paper facestock, metering the adhesive off with a knife to a coat weight of 22 grams per square meter, and curing the adhesive in an oven at 180°F. Some of the laminate samples are aged at room temperature for one day, one week or three weeks as indicated below. Also, some of the laminate samples are heat aged for one day at 158°F, or for one or three weeks at 140°F, as indicated below.

Tests are performed to measure the following:

(1) 90° Release Force: Force required to remove the release coated liner from the adhesive coated facestock at a 90° angle and at a prescribed rate of either 12 inches per minute (ipm) or 300 ipm. The results are given in grams release force (grf).

(2) Loop Tack: Force resisting peeling of a tape at 90° from a standard surface upon which it has been applied under no other pressure than the weight of the tape itself using an Instron tensile tester. The results are given in grf.

(3) F/L Imass: Force in grams used to pull the facestock from the release coated liner measured at a speed of 0.05 m/s or 2.54 m/s as indicated below.

(4) L/F Imass: Force in grams used to pull the release coated liner from the facestock at a speed of 0.05 m/s or 2.54 m/s as indicated below.

The results of these tests are indicated in the table below:

Aging/Test Method	Sample B		Sample A		Sample A	
	JR Camus MG		JR Camus MG		Otis UV 350	
Wet Cast 5730	RT	Heat Age	RT	Heat Age	RT	Heat Age
90° Release (300 ipm)						
1 Day	64	98	43	45	46	57
1 Week	72	91	43	42	50	52
3 Weeks	103	132	41	44	54	54
90° Release (12 ipm)						
1 Day	30	59	16	21	15	20
1 Week	36	72	17	19	15	20
3 Weeks	52	124	14	23	14	25
Loop Tack						
1 Day	2.23	2.12	2.07	2.27	2.19	2.67
1 Week	1.89	2.22	2.07	2.46	2.57	2.19
3 Weeks	2.21	2.24	2.02	2.14	2.10	2.66
F/L Imass (0.05 m/s)						
1 Day	47	69	21	30	25	27
1 Week	54	66	24	25	26	32
3 Weeks	68	106	21	21	27	31

F/L Imass
(2.54 m/s)

5	1 Day	76	90	50	48	51	54
	1 Week	66	94	49	47	56	56
	3 Weeks	69	104	46	48	54	49

L/F Imass
(0.05 m/s)

10	1 Day	121	PT*	46	69	39	40
	1 Week	108	PT	44	55	34	36
	3 Weeks	230	PT	41	98	38	41

L/F Imass
(2.54 m/s)

15	1 Day	287	PT	120	123	43	48
	1 Weeks	276	PT	118	115	48	46
	3 Weeks	PT	PT	102	197	53	65

*PT means that the paper tore.

The foregoing results indicate that the performance of the inventive composition (Sample A) is superior to the performance of the control sample (Sample B) when used with the JR Camus MG release liner sheet. Also, by virtue of the use of the inventive composition (Sample A) equivalent results are obtained with the conventional paper release liner (JR Camus MG) as with the premium specially made paper (Otis UV 350).

Example 2

A pigment slip is prepared by dispersing 5 grams of Martifil P2 (a product of Pluss-Stauffer identified as aluminum trihydrate) in 20 grams of n-butyl lactate. The pigment slip has a 25% by weight solids content. A release coating composition is prepared by mixing 20 grams of UV 9315 (a product of General Electric identified as a epoxy functional polyorganosiloxane) and 0.4 gram of UV 9380C (a product of General Electric identified as a photoinitiator). One gram of the pigment slip is mixed with the release coating composition to provide a solids containing release coating composition. The solids containing release coating composition is drawn down on a 44# paper liner that has been coated with a layer of polyolefin. The coat weight is 1 gsm. The coating is cured by passing the release coated liner through a Fusion benchtop curing unit one time at a rate of 50 feet per minute using one 300 watt fusion "H" bulb.

Example 3

A pigment slip is prepared by dispersing 5 grams of Martifil P2 in 10 grams of Dowanol (a product of Dow identified as dipropylene glycol n-butyl ether). The resulting pigment slip has a solids content of 33% by weight. A release coating composition is prepared by mixing 18 grams of UV 9315 and 0.5 gram of UV 9380C. Four grams of the pigment slip are mixed with the release coating composition to provide a solids containing release coating composition. The solids containing release coating composition is drawn down on a 44# paper liner that has been coated with a layer of polyolefin to a coat weight of 1.3 gsm. The coating is cured using the same procedure as in Example 2.

Example 4

A release coating composition is prepared by mixing 20 grams of UV 9315 with 0.5 gram of UV 9380C. Five grams of Translink 77 are added to the release coating composition to provide a solids containing release coating composition. The solids content is 25% by weight. The solids containing release coating is drawn down on PD 350 MF (a product of Otis Specialty Papers identified as a 42# paper liner specially designed for UV curing) at a coat weight of 1.3 gsm. The drawn down coating is cured using the same procedure as in Example 2.

Example 5

A pigment slip is prepared by dispersing 5 grams of Martifil P2 into 10 grams of di-acetone alcohol. The pigment slip has a 33% by weight solids content. A release coating composition is prepared by mixing 20 grams of UV 9315 and 0.4 grams of UV 9380C. Two grams of the pigment slip are added to the release coating composition to provide a solids containing release coating composition. The solids containing release coating composition is drawn down on a 44# paper liner that has coated with a polyolefin. The coat weight is 1 gsm. The coating is cured using the same procedure as in Example 2.

Example 6

Particulate solids containing release coating compositions having the formulations indicated below are prepared (all numerical values in the table below are in grams):

	<u>Ingredients</u>	<u>Sample</u>		
		<u>A</u>	<u>B</u>	<u>C</u>
5	UV 9400	35	25	25
	UV 9380C	1.3	1.3	1.3
	UV 9430	2.5	2.5	2.5
10	UV 9330 (product of GE identified as a release additive)	12.5	12.5	12.5
	Translink 77	--	--	10
	Martinal 104LE	--	10	--

Sample A is a control sample wherein no particulate solids are added. Samples B and C are representative of the invention. Each of the Samples A-C are drawn down on sheets of 40# machine glazed paper at a coat weight of 1.3 gsm using a lamination pressure of 40 psi. The drawn-down sheets are cured under a fusion mercury lamp at 300 watts per inch using one pass at a rate of 250 fpm. The 90° release force is measured for samples of each of the foregoing using an adhesive tape, the adhesive being a hot melt styrene butadiene rubber adhesive. Samples of each of the foregoing cured sheets are aged for 24 hours at room temperature (RT) or 158°F and then tested for 90° release force. The results are indicated below.

		<u>Sample</u>		
		<u>A</u>	<u>B</u>	<u>C</u>
25	90° Release Force, grams	22	36	23

90° Release Force after aging,
grams

RT	60	64	63
158°F	72	84	88

5

Example 7

Release coating compositions having the formulations indicated below are prepared (all numerical values being in percent by weight except for the amount of UV 9380 which is expressed as 2.5 parts per weight based on 100 parts by weight of the remaining formulation):

10

IngredientsSampleAB

UV 9400	70%	50%
UV 9380	2.5 parts	2.5 parts
UV 9330	5%	5%
UV 9430	25%	25%
Translink 77	--	20%

15

20

Sample B is representative of the invention and Sample A is a control provided for purposes of comparison. Each of the samples are coated on four different types of conventional paper release liners, as well as on Otis UV 350 which, as indicated above, is a premium liner paper specially developed for use with epoxy-based UV silicones. The conventional paper release liners are as follows:

25

Warren:	a product of Warren identified as a 39# soft-nip calendered kraft paper
Fraser:	a product of Fraser identified as a 40# super calendered kraft paper
Simpson:	a product of Simpson identified as a 41# premium super calendered kraft paper

Rhineland: Rhineland RL-20 which is a product of Rhineland identified as a 42# super calendered kraft paper.

The coat weight of each sample is 1.3 grams per square meter. The samples are cured with one pass through a Fusion bench top model cure unit equipped with one 300 watt Fusion "H" bulb at a rate of 200 feet per minute. The cured samples are adhered to an acrylic adhesive tape and the resulting laminates are aged for one day at room temperature (RT) or 158°F as indicated below. The 90° Release Force at a rate of 300 ipm is measured for each sample with the results being indicated below (all numerical values being in grams of force except for the aging temperature which is in °F):

<u>Sample</u>	<u>Aging</u>	<u>Warren</u>	<u>Fraser</u>	<u>Simpson</u>	<u>Rhineland</u>	Otis <u>UV 350</u>
A	RT	53	52	51	55	45
A	158°F	123	71	98	89	68
B	RT	46	45	48	49	42
B	158°F	64	57	59	65	48

The foregoing results indicate that comparable results are achieved with conventional release liners using Sample B (the invention) as compared to the Sample A (the control) and the specially formulated Otis UV 350 release liner paper.

While the invention has been explained in relation to its preferred embodiments, it is to be understood that various modifications thereof will become apparent to those skilled in the art upon reading the specification. Therefore, it is to be understood that the invention disclosed herein is intended to cover such modifications as fall within the scope of the appended claims.

Claims

1. A release composition, comprising: a radiation-curable polyorganosiloxane and surface treated particulate solids.

2. The composition of claim 1 wherein said composition further comprises a photoinitiator.

3. The composition of claim 1 wherein said polyorganosiloxane contains acryloxy groups, methacryloxy groups, or combinations thereof.

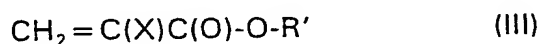
4. The composition of claim 1 wherein said polyorganosiloxane is represented by the formula



wherein in Formula (I), each R is acryloxy, methacryloxy, a non-substituted monovalent hydrocarbon group containing from 1 to about 20 carbon atoms or a substituted monovalent hydrocarbon group wherein the substituents are selected from the group consisting of chloro-, fluoro-, cyano-, amido-, nitro-, ureido-, isocyanato-, carbalkoxy-, hydroxy-, acryloxy, and methacryloxy; n has an average value of about 1.8 to about 2.2; and m has an average value greater than 2; the polyorganosiloxane containing an average of at least one R group which contains an acryloxy or methacryloxy group.

5. The composition of claim 4 wherein the substituents represented by R in Formula (I) can be aliphatic groups, cycloaliphatic groups, aryl groups, or alkenyl groups.

6. The composition of claim 4 wherein the R groups in Formula (I) have the structure



wherein in Formula (III), R' is a divalent hydrocarbon group of from 1 to about 15 carbon atoms or an oxyalkylene group containing from 1 to about 4 carbon atoms in the alkylene moiety.

7. The composition of claim 1 wherein said polyorganosiloxane contains acryloxy or methacryloxy groups, and said composition further

comprises acrylated or methacrylated organic polyhydroxy compounds or polyamino compounds.

8. The composition of claim 1 wherein said composition further comprises a monoacrylate or monomethacrylate compound.

5 9. The composition of claim 1 wherein said polyorganosiloxane is an epoxypolyorganosiloxane.

10. The composition of claim 1 wherein said polyorganosiloxane is a compound represented by the formula

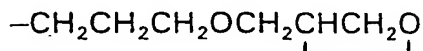
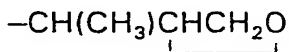
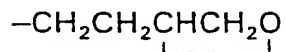


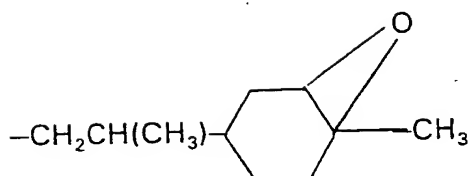
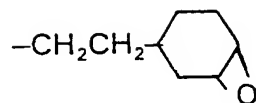
10 wherein in Formula IV: each R is independently a hydrocarbon group of 1 to about 18 carbon atoms; E is a monovalent epoxy containing hydrocarbon group; G is a silyl group represented by the formula $\text{R}_3\text{Si}-$ or $\text{R}_2\text{ESi}-$; a is a number in the range of about 10 to about 300; and b is a number in the range of about 2 to about 10.

15 11. The composition of claim 10 wherein E contains at least one epoxy group, the remainder comprised of carbon and hydrogen.

12. The composition of claim 11 wherein E also contains an ether or carbonyl oxygen.

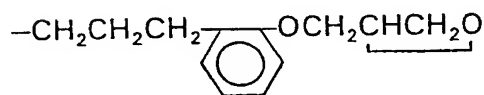
20 13. The composition of claim 10 wherein E is represented by the formula





5

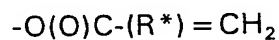
or



14. The composition of claim 1 wherein said release composition further comprises an organosiloxane copolymer represented by the formula



wherein in Formula (V), each R is independently a hydrocarbon group or a group represented by the formula



wherein R* is hydrogen or a methyl or ethyl group; x is a number from about 0.25 to about 75; and y is a number in the range of about 1 to about 56.

15. The composition of claim 2 wherein said photoinitiator is a benzy ketal, benzoin ether, acetophenone derivative, ketoxime ether, benzophenone, benzoxanthone or thioxanthone.

16. The composition of claim 1 wherein said particulate solids are selected from the group consisting of calcined clay, aluminum trihydrate, and mixtures thereof.

17. The composition of claim 1 wherein said particulate solids
5 comprise vinyl treated calcined clay.

18. The composition of claim 1 wherein said particulate solids are surface treated by contacting said particulate solids with a coupling agent, reactive diluent, or mixture thereof.

19. The composition of claim 1 wherein said particulate solids
10 are surface treated by contacting said particulate solids with a compound selected from the group consisting of dipropylene glycol n-butyl ether, n-butyl lactone, di-acetone alcohol, and mixtures of two or more thereof.

20. A method of making a release coated substrate which comprises applying a coating of the composition of claim 1 to a substrate; and
15 curing the coating on the substrate by exposing the coating to radiation.

21. The method of claim 20 wherein the composition is cured with ultraviolet light.

22. A release-coated article comprising a substrate which has been coated with the release composition of claim 1 and which has been cured
20 by exposure to radiation.

23. The release-coated article of claim 22 wherein the substrate is paper.

24. A multilayer article, comprising:
(a) a first substrate;
25 (b) a second substrate;
(c) a release layer comprising the release composition of claim 1 which has been cured by exposure to radiation; and
(d) a pressure-sensitive adhesive layer, wherein the release layer (c) is interposed between the first substrate and the layer of
30 pressure-sensitive adhesive (d) and is preferentially adherent to the first substrate, and the pressure sensitive adhesive layer (d) is interposed between

the release layer and the second substrate and is preferentially adherent to the second substrate.

25. The multilayer article of claim 24 wherein the first and second substrates are paper.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 98/20403

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C08K9/00 C08L83/04 C09D183/06 C09J7/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C08K C08L C09D C09J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 95 23694 A (AVERY DENNISON CORPORATION) 8 September 1995 see page 10, line 7 - line 11 see claims 1,5,6 ----	1-8, 15, 20-25
A	EP 0 464 706 A (TOSHIBA SILICONE CO.) 8 January 1992 see page 4, line 16 - line 22 see example 6 ----	1, 2, 10-15, 20-25
A	DE 26 41 699 A (WACKER) 23 March 1978 see claims 1,4 ----	1, 16-19
A	US 5 061 740 A (H. INOMATA) 29 October 1991 see column 10, line 5 see claim 1 -----	1, 16-19



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

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Date of the actual completion of the international search

4 February 1999

Date of mailing of the international search report

12/02/1999

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INTERNATIONAL SEARCH REPORT

Information on patent family members

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